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High Carbon-High porous SiOC glasses for room temperature NO₂ sensing

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Abstract

Porous SiOC is proposed as suitable material for gas sensing applications, exploiting its high surface area and high carbon content. The typical high electrical resistance of SiOC, which prevented till now its exploitation to develop conductometric devices, is solved through a proper control of its carbon content and thermal treatments. The developed gas sensors showed high sensitivity to NO₂ at room temperature and up to 400°C. We believe that this new kind of nanoporous ceramic gas sensors can give a new perspective for application of ceramic materials in gas sensing field.

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Keywords: SiOC; RT gas sensing; NO₂; porous ceramics; Carbon rich

1. Introduction

The common operating temperature for metal oxides to respond NO₂ is between 300-500°C [1-2]. However, in many cases, the high-temperature operation is not favorable, i.e. in an explosive environment [2]. In this study, we propose porous SiOC glasses, a ternary system of Si-O-C, as a NO₂ sensing material at low temperatures. SiOC is known for its high temperature stability but it has never been considered as sensing material due to its high resistivity. In this work we show that the proper control of its structure and stoichiometry allows obtaining resistance

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values suited for gas sensing application. Indeed, the functional characterization of the prepared sensor devices demonstrates that porous SiOC is a possible candidate for room temperature NO₂ sensing.

2. Experimental

Porous SiOC ceramics starting from aerogels are prepared by a polymer derived method. In this simple process, highly porous ambigels are successfully employed as precursors to get porous SiOC with high surface area [3]. Final SiOC composition so as the resistivity of the final ceramic can be adjusted by changing starting gel (xerogels) composition and the pyrolysis temperature which gives great flexibility to change the sensitivity of the sensor. Responses are tested by *in situ* DC conductance measurements from RT to 500°C with 30% humidity.

3. Results and discussion

Porous SiOC ceramics are prepared, starting from aerogels, by a polymer pyrolysis method [3]. In this simple process, highly porous aerogels are successfully employed as precursors to get porous SiOC with specific surface area as high as 588 m²/g. Final SiOC composition and accordingly the resistivity of the final ceramic- is adjusted by changing the starting aerogel composition and the pyrolysis temperature which gives great flexibility to change the sensitivity of the sensor. In this work, we increase the C content to increase the conductivity and to shift NO₂ response to room temperature compared to low carbon-low porosity SiOC glasses [4].

The gas sensing properties of SiOC are investigated from room temperature to 500°C. The material reveals high selectivity and good sensitivity towards NO₂ (5-10 ppm) with null response to H₂. The gas response to NO₂ at room temperature is quite remarkable. As the operating temperature increases, the response to NO₂ decreases and totally disappears at 400°C. Dynamic gas responses to NO₂ (5 ppm) at RT-250°C are plotted in Figure 1. Although response is the highest at room temperature, the recovery is irreversible at this temperature.

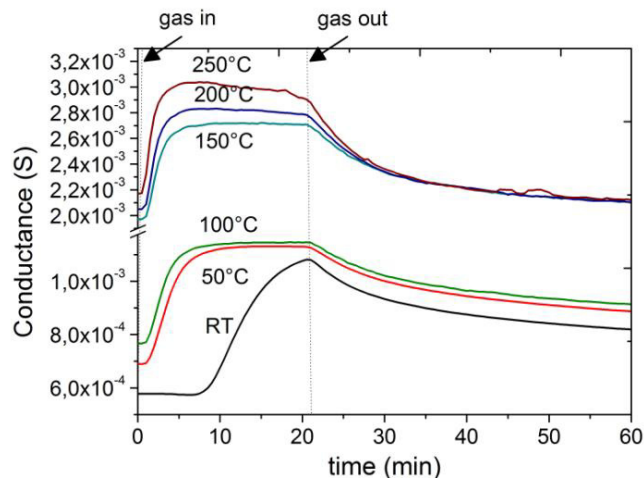


Fig. 1. Dynamic response exhibited by SiOC sensors to 5 ppm NO₂ from room temperature to 250°C

As temperature increases, the sample responds faster and recovery changes from irreversible to reversible. The response time, recovery time and response as a function of operation temperature is plotted in Figure 2-3. The sample starts giving response to H_2 after $400^\circ C$ only when SiOC loses its sensitivity towards NO_2 (not shown).

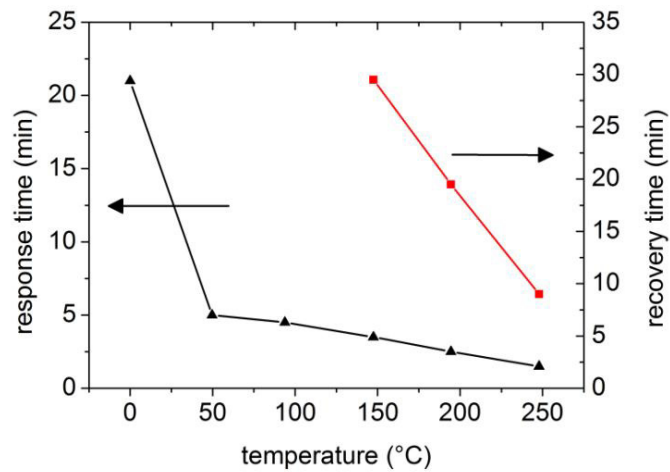


Fig. 2. Response and recovery time of the sample to 5 ppm NO_2 from room temperature to $250^\circ C$

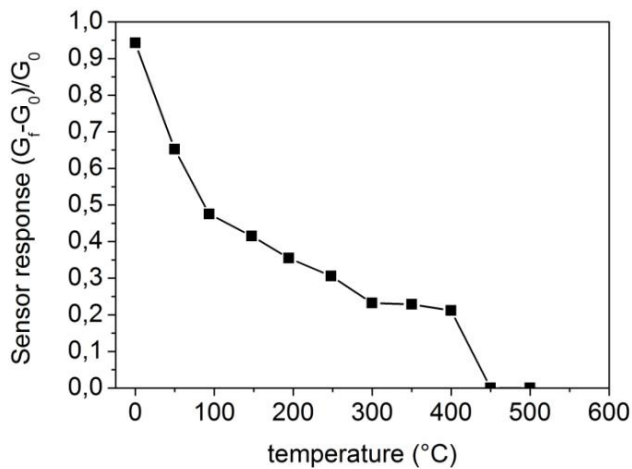


Fig. 3. NO_2 responses at RT- $500^\circ C$

4. Conclusions

SiOC glasses show two distinct behaviors: $T < 400^\circ C$, they are very sensitive to NO_2 and $T > 400^\circ C$ the NO_2 sensitivity disappears and they response to H_2 . It is possible to tailor the sensing properties playing with Carbon

content in the starting precursor. Increasing the porosity and carbon content in the structure resulted in high conductivity and NO₂ response to shift to RT.

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